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Reaction of the Diisopropylaminochlorophosphenium Cation with Crotonaldehyde Dimethylhydrazone and Acetone Azine

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ABSTRACT

The phosphenium ion $[(\text{i-}Pr_2N)ClP]^+$ **(1)** *reacts with crotonaldehyde dimethylhydrazone* **(2)** *to afford a product with a* C_3NP *ring system* **(4)**. *The reaction of* **1** *with acetone azine* **(3)** *results in a novel tricyclic compound* **(6)** *which features a* $C_2N_2P_2$ *and two* C_2N_2P *rings. The structures of* **4** *and* **6** *were established by X-ray crystallography. Compound* **4**, $C_{12}H_{26}AlCl_3N_3OP$, *crystallizes in the monoclinic space group* $P2_1/n$ *with* $Z = 4$, $a = 15.400(6)$, $b = 14.442(4)$, $c = 9.206(3)$ Å, *and* $\beta = 93.33(3)°$. *Compound* **6**, $C_{12}H_{22}Al_2Cl_6N_4O_2P_2$, *crystallizes in the triclinic group* $P\bar{1}$ *with* $Z = 1$, $a = 8.556(1)$, $b = 9.782(1)$, $c = 8.119(1)$ Å, $\alpha = 94.48(1)$, $\beta = 104.97(1)$, *and* $\gamma = 78.35(1)°$.

INTRODUCTION

It has been known for over three decades that the reaction of conjugated dienes with dihalophosphines represents a useful route to phosphorus heterocycles [1]. In the 1970's Kashman and coworkers reported that aluminum halide complexes of the type $RPX_2 \cdot AlX_3$ undergo comparable reactions with 1,3 and other dienes [2]. More recently, SooHoo and Baxter [3] and ourselves [4] discovered that these diene reactions can be greatly accelerated if stabilized phosphenium ions, $[R_1R_2P]^+$, are used in place of dihalophosphines. The use of phosphenium ions is particularly advantageous for sterically encumbered dienes. With a view to extending this method of phosphorus heterocycle synthesis, we decided to investigate the reaction of $[(i\text{-}Pr_2N)ClP]^+$ **(1)** with heteroatom analogs of dienes. Crotonaldehyde dimethylhydrazone, $MeCH{=}CHCH{=}NNMe_2$ **(2)**, and acetone azine, $Me_2C{=}NN{=}CMe_2$ **(3)**, were chosen because they represent systems where one and two C=C bonds are replaced by C=N moieties.

RESULTS AND DISCUSSION

The reaction of the $[AlCl_4]^-$ salt of **1** with crotonaldehyde dimethylhydrazone **(2)** affords the cyclic phosphine oxide **4** which is complexed to an $AlCl_3$ unit (Scheme 1). We presume that **4** is produced by hydrolysis of the cyclic chlorophosphonium salt **5**. Interestingly, when stringent measures were taken to remove traces of water from **2** (or **3**) it was not possible to obtain tractable products. The identity of **4** was established by an X-ray structure analysis. Bond lengths and bond angles are listed in Tables 1 and 2, respectively, and the positional parameters are listed in Table 3. The structure analysis confirms that the carbon–carbon double bond is loca-

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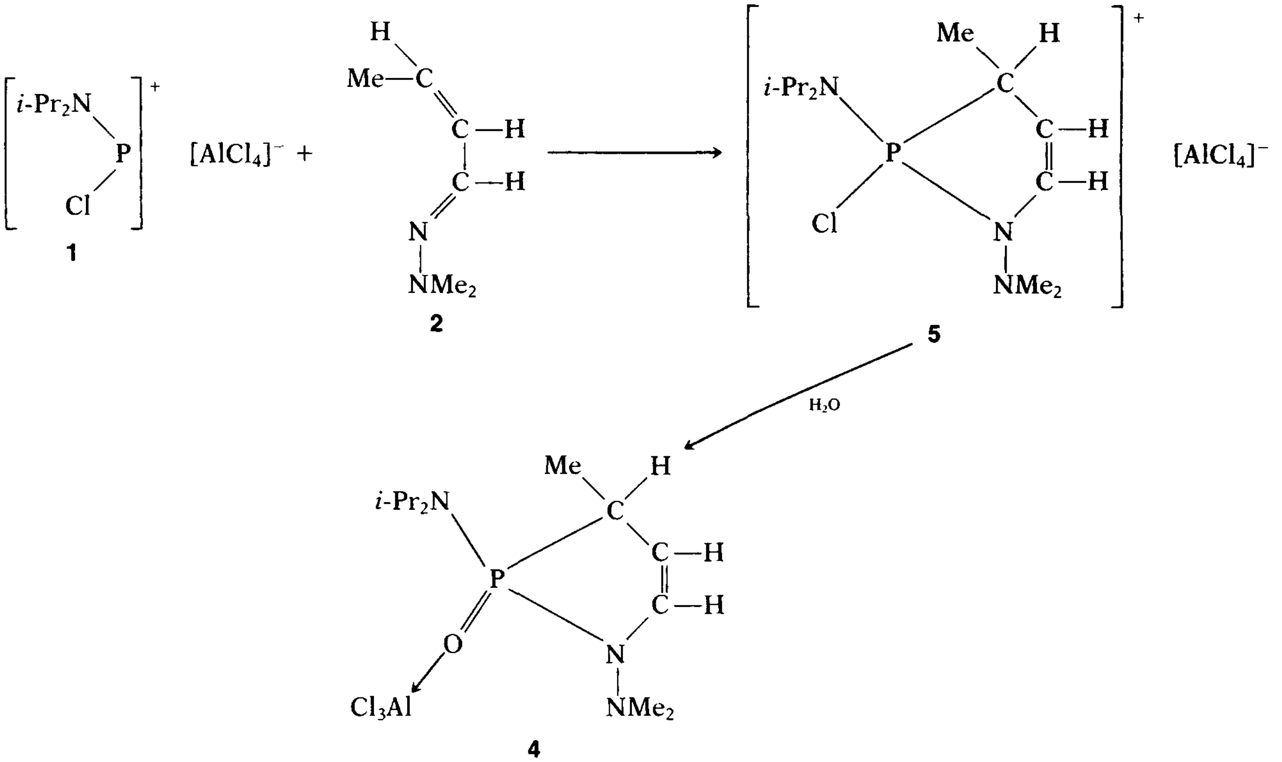

SCHEME 1

ted between C3 and C4 (Figure 1) and reveals that an $AlCl_3$ unit is coordinated to the phosphoryl group. The geometry of the *i*-Pr_2NP moiety of **4** is very similar to that of $[(i\text{-}Pr_2N)_2P]^+$ [5] in that nitrogen atom N3 adopts a trigonal planar configuration and the P–N3 bond length is short (~0.01 Å longer than in the phosphenium ion). By contrast, the geometry at N2 is tetrahedral and the N1–N2 distance corresponds to a bond order of unity.

As in the case of the reaction of phosphenium ions with 1,3-dienes [3,4], **1** reacts with **2** via 1,4-addition. It has been pointed out previously [6] that such an addition can take place by a concerted [2 + 4] chelotropic process or by a two-step mechanism in which an initial 1,2-adduct rearranges to the 1,4-product. Biradical processes are unlikely because MO calculations indicate that phosphenium ions are ground state singlets [7].

The reaction of **1** with acetone azine took an unexpected course. At the present time we do not have any mechanistic information pertinent to this unusual reaction; hence, the sequence of reactions suggested in Scheme 2 should be regarded as

TABLE 1 Bond Lengths for **4**

Atom 1	*Atom 2*	*Bond length (Å)*[a]	*Atom 1*	*Atom 2*	*Bond length (Å)*[a]
Cl1	Al	2.117(1)	N2	C6	1.458(4)
Cl2	Al	2.120(1)	N3	C7	1.494(2)
Cl3	Al	2.112(1)	N3	C10	1.493(2)
P	O	1.515(1)	C1	C2	1.530(3)
P	N1	1.645(2)	C2	C3	1.501(3)
P	N3	1.622(1)	C3	C4	1.290(3)
P	C2	1.818(2)	C7	C8	1.512(4)
Al	O	1.748(1)	C7	C9	1.506(4)
N1	N2	1.410(2)	C10	C11	1.497(4)
N1	C4	1.422(3)	C10	C12	1.530(3)
N2	C5	1.479(3)			

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[a] Values in parentheses are estimated standard deviations in the least significant digits.

TABLE 2 Bond Angles for **4**

Bonded atoms	*Bond angle* (°)^a	*Bonded atoms*	*Bond angle* (°)^a
O-P-N1	114.74(8)	N1-N2-C6	110.2(2)
O-P-N3	107.05(7)	C5-N2-C6	111.5(3)
O-P-C2	108.61(9)	P-N3-C7	122.9(1)
N1-P-N3	110.84(8)	P-N3-C10	120.5(1)
N1-P-C2	94.11(9)	C7-N3-C10	116.5(2)
N3-P-C2	121.44(9)	P-C2-C1	116.5(2)
Cl1-Al-Cl2	112.25(4)	P-C2-C3	102.1(2)
Cl1-Al-Cl3	110.85(4)	C1-C2-C3	112.9(2)
Cl1-Al-O	108.07(5)	C2-C3-C4	115.3(2)
Cl2-Al-Cl3	110.12(3)	N1-C4-C3	115.2(2)
Cl2-Al-O	106.32(6)	N3-C7-C8	113.8(2)
Cl3-Al-O	109.06(5)	N3-C7-C9	112.3(2)
P-O-Al	152.95(9)	C8-C7-C9	113.2(3)
P-N1-N2	121.8(1)	N3-C10-C11	111.6(2)
P-N1-C4	110.6(2)	N3-C10-C12	112.2(2)
N2-N1-C4	125.1(2)	C11-C10-C12	111.1(2)
N1-N2-C5	111.0(2)		

[a] Values in parentheses are estimated standard deviations in the least significant digits.

tentative. Since phosphenium ions are known to be powerful Lewis acids [6], we propose that the first step of the reaction is formation of a donor–acceptor complex. Note that in the second step, formation of the PN_2C_2 ring is accomplished by insertion of the phosphenium moiety into a C—H bond of a methyl group. Intramolecular carbon—hydrogen insertion reactions of this general type have been observed previously [8]. In the next three steps, we propose elimination of *i*-Pr_2NH, followed by OH^- attack to afford an intramolecularly stabilized R—P=O species which undergoes dimerization to afford the final product, **6**. As in the case of the crotonaldehyde dimethylhydrazone, $AlCl_3$ units remain attached to the phosphoryl groups. The structure of **6** was determined by x-ray

FIGURE 1 Structure of **4** showing the atom numbering scheme.

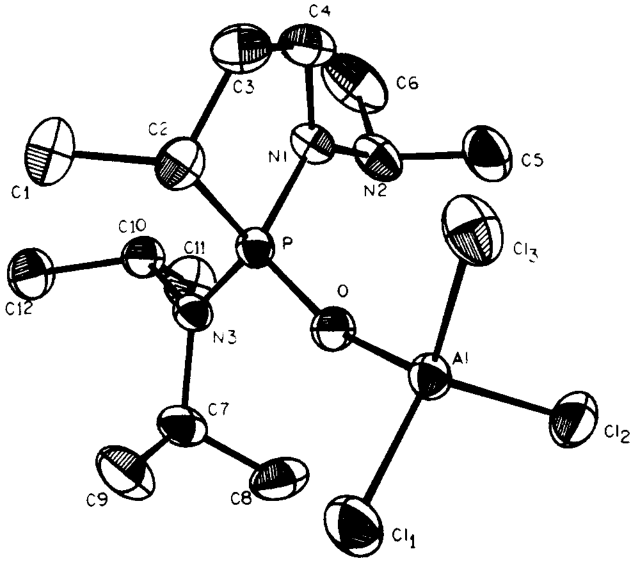
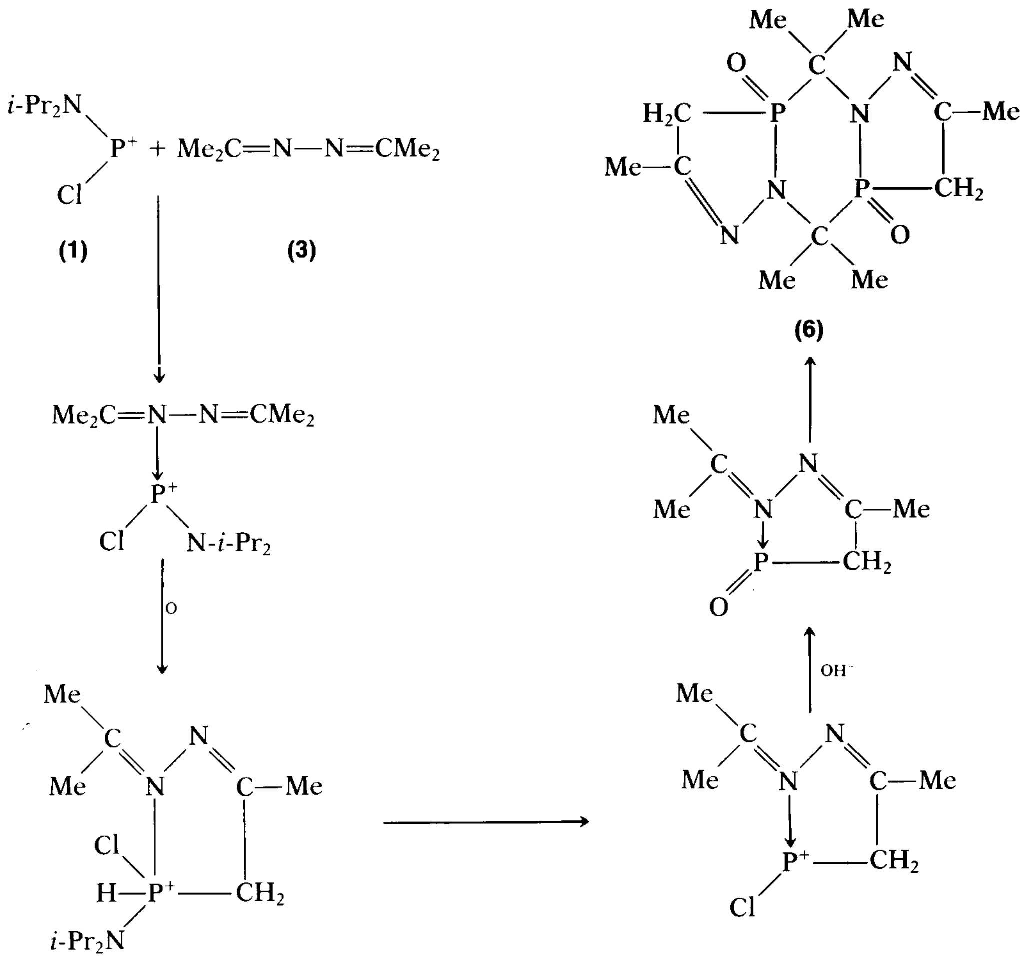


TABLE 3 Positional Parameters and Their Estimated Standard Deviations for **4**

Atom	*x*^{a}	*y*^{a}	*z*^{a}	*B*(Å^2)^{a,b}
CL1	0.68831(8)	0.3878(1)	0.2687(1)	7.29(3)
Cl2	0.54711(8)	0.20235(9)	0.1786(1)	5.80(3)
Cl3	0.46937(7)	0.39955(8)	0.3428(1)	6.12(3)
P	0.59260(6)	0.24866(7)	0.6573(1)	3.15(2)
Al	0.57800(7)	0.31165(9)	0.3265(1)	3.75(2)
O	0.6027(1)	0.2597(2)	0.4954(2)	3.99(5)
N1	0.5013(2)	0.1991(2)	0.6999(3)	3.71(6)
N2	0.4821(2)	0.1063(2)	0.6632(4)	4.89(8)
N3	0.6761(2)	0.1903(2)	0.7222(3)	3.52(6)
C1	0.6159(3)	0.3904(3)	0.8717(5)	6.2(1)
C2	0.5647(3)	0.3605(3)	0.7322(4)	4.27(9)
C3	0.4691(3)	0.3499(3)	0.7518(5)	5.5(1)
C4	0.4392(2)	0.2669(3)	0.7360(4)	4.9(1)
C5	0.4237(3)	0.1009(4)	0.5300(6)	7.0(1)
C6	0.4449(3)	0.0591(4)	0.7850(7)	7.9(1)
C7	0.7592(2)	0.1839(3)	0.6468(4)	4.83(9)
C8	0.7530(3)	0.1245(4)	0.5114(5)	6.5(1)
C9	0.7988(3)	0.2776(4)	0.6225(6)	7.0(1)
C10	0.6741(2)	0.1431(3)	0.8662(4)	4.50(9)
C11	0.6822(3)	0.0402(3)	0.8519(5)	6.4(1)
C12	0.7430(3)	0.1814(4)	0.9768(5)	6.4(1)
H1A	0.601(2)	0.348(3)	0.952(4)	7(1)*
H1B	0.587(3)	0.448(3)	0.919(5)	8(1)*
H1C	0.675(2)	0.393(3)	0.859(4)	6(1)*
H2	0.572(2)	0.404(2)	0.656(3)	2.8(7)*
H3	0.438(3)	0.398(3)	0.782(4)	7(1)*
H4	0.393(2)	0.245(3)	0.758(4)	4.9(9)*
H5A	0.367(2)	0.123(3)	0.545(4)	6(1)*
H5B	0.415(3)	0.033(3)	0.507(5)	8(1)*
H5C	0.453(3)	0.136(3)	0.450(5)	8(1)*
H6B	0.389(3)	0.083(3)	0.815(5)	8(1)*
H6A	0.479(2)	0.056(3)	0.862(4)	6(1)*
H6C	0.445(3)	−0.012(4)	0.763(5)	11(2)*
H7	0.792(2)	0.148(2)	0.708(3)	3.7(7)*
H8B	0.730(3)	0.155(3)	0.431(4)	7(1)*
H8A	0.811(3)	0.111(3)	0.473(4)	8(1)*
H8C	0.731(3)	0.066(3)	0.537(5)	8(1)*
H9B	0.769(3)	0.319(3)	0.545(5)	8(1)*
H9C	0.852(3)	0.269(3)	0.576(5)	9(1)*
H9A	0.802(3)	0.316(3)	0.706(4)	7(1)*
H10	0.617(2)	0.156(2)	0.907(3)	3.2(7)*
H11C	0.648(2)	0.014(3)	0.792(4)	6(1)*
H11A	0.676(3)	0.004(3)	0.950(4)	8(1)*
H11B	0.740(3)	0.023(3)	0.818(4)	8(1)*
H12A	0.736(2)	0.249(3)	0.996(4)	7(1)*
H12C	0.730(3)	0.149(3)	1.072(4)	8(1)*
H12B	0.797(2)	0.165(3)	0.956(4)	6(1)*

[a] Values in parentheses are estimated standard deviations.

[b] Starred atoms were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as: (4/3) • [a2*B(1,1) + b2*B(2,2) + C2*B(3,3) + ab(cos gamma)*B(1,2) + ac(cos beta)*B(1,3) + bc(cos alpha)*B(2,3)].



SCHEME 2. $AlCl_3$ units on P=O bonds not shown.

crystallography. Bond lengths and bond angles are listed in Tables 4 and 5, respectively, and the structure is illustrated in Figure 2. The positional parameters are listed in Table 6. Individual molecules of **6** reside on a center of symmetry. It is clear from Table 2 that the carbon–nitrogen double bonds are located between N1 and C2 and N1′ and C2′.

TABLE 4 Bond Lengths for **6**

Bond	*Length (Å)*[a]
Al–Cl1	2.105(1)
Al–Cl2	2.131(1)
Al–Cl3	2.104(1)
Al–O	1.764(2)
P–O	1.505(2)
P–N2	1.645(2)
P–C1	1.798(2)
P–C4	1.835(2)
N1–N2	1.443(2)
N1–C2	1.283(3)
N2–C4	1.493(3)
C1–C2	1.512(4)
C2–C3	1.500(3)
C4–C5	1.522(4)
C4–C6	1.506(4)

[a] Values in parentheses are estimated standard deviations in the least significant digits.

EXPERIMENTAL

Reaction of [(i-Pr_2N)ClP][$AlCl_4$] *with Crotonaldehyde Dimethylhydrazone and Acetone Azine*

A solution of [(*i*-Pr_2N)ClP][$AlCl_4$] was made by treatment of 1.95 g (9.7 mmol) of *i*-Pr_2NPCl_2 in 30 mL of degassed CH_2Cl_2 with 1.37 g (5.0 mmol) of freshly sublimed Al_2Cl_6 at −78°C [8]. The reaction mixture warmed slowly to room temperature and was subsequently stirred for 3 h. After the phosphenium ion solution was recooled to −78°C, crotonaldehyde dimethylhydrazone or acetone azine (9.1

TABLE 5 Bond Angles for **6**

Bond	Angle (°)^a
Cl1-Al-Cl2	110.98(5)
Cl1-Al-Cl3	111.90(5)
Cl1-Al-O	106.82(8)
Cl2-Al-Cl3	112.74(5)
Cl2-Al-O	105.61(7)
Cl3-Al-O	108.36(7)
O-P-N2	115.8(1)
O-P-C1	113.1(1)
O-P-C4	109.1(1)
N1-N2-C4	115.2(1)
N1-N2-P	111.5(2)
N1-C2-C3	120.0(3)
N1-C2-C1	118.8(2)
N2-P-C1	92.6(1)
N2-P-C4	107.7(1)
N2-C4-C5	112.1(2)
N2-C4-C6	110.0(2)
N2-C4-P	101.0(1)
N2-N1-C2	109.4(2)
P-N2-C4	128.3(1)
P-O-Al	155.1(1)
P-C1-C2	99.8(2)
P-C4-C5	111.1(2)
P-C4-C6	109.1(2)
C1-P-C4	118.0(1)
C1-C2-C3	121.2(3)
C5-C4-C6	112.9(3)

[a] Values in parentheses are estimated standard deviations in the least significant digits.

TABLE 6 Positional Parameters and Their Estimated Standard Deviations for **6**

Atom	x^a	y^a	z^a	$B(A^2)^{a,b}$
Al	0.7967(2)	0.2757(2)	0.9018(2)	3.69(4)
Cl1	0.9376(2)	0.3638(2)	0.1212(3)	5.43(4)
Cl2	0.6422(3)	0.4341(2)	0.7362(2)	6.32(5)
Cl3	1.0553(2)	−0.1264(2)	1.2222(3)	6.62(5)
P	0.4965(2)	0.1640(1)	0.9760(2)	2.67(3)
O	0.6619(5)	0.1913(4)	0.9703(5)	3.75(9)
N1	1.3207(6)	0.1170(5)	0.6787(5)	3.5(1)
N2	1.4207(5)	0.0501(5)	0.8330(5)	2.88(9)
C1	1.3295(7)	0.3036(6)	0.8912(7)	3.4(1)
C2	1.2750(7)	0.2474(6)	0.7109(7)	3.6(1)
C3	0.1633(9)	0.3399(8)	−0.4275(8)	5.8(2)
C4	1.5109(7)	0.1015(6)	1.1875(6)	3.0(1)
C5	1.3421(8)	0.1255(6)	1.2253(7)	4.3(1)
C6	1.6333(9)	0.1696(7)	1.3188(8)	5.0(2)
H1	0.233(7)	0.306(6)	−0.056(8)	5(2)*
H2	0.376(9)	0.400(8)	−0.089(9)	3(2)*
H3	0.073(8)	0.378(7)	−0.383(8)	6(2)*
H4	0.227(8)	0.410(7)	−0.436(8)	8(2)*
H5	0.139(9)	0.291(8)	−0.55(1)	10(2)*
H6	0.344(7)	0.086(6)	0.322(8)	5(2)*
H7	0.330(7)	0.226(6)	0.249(7)	4(1)*
H8	0.252(8)	0.084(7)	0.136(8)	6(2)*
H9	0.740(8)	0.147(7)	0.304(8)	5(2)*
H10	0.600(6)	0.261(5)	0.309(7)	3(1)*
H11	0.629(7)	0.145(6)	0.414(7)	4(1)*

[a] Values in parentheses are estimated standard deviations.
[b] Starred atoms were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as: (4/3) * [a2*B(1,1) + b2*B(2,2) + c2*B(3,3) + ab(cos gamma)*B(1,2) + ac(cos beta)*B(1,3) + bc(cos alpha)*B(2,3)].

mmol) was added dropwise from a syringe. The reaction mixtures warmed to room temperature with stirring, during which time they assumed a deep orange color. Careful layering of hexane onto this reaction mixture and slow diffusion of the hexane into the CH_2Cl_2 layer resulted, after 5 weeks, in the formation of X-ray quality crystals of **4** and **6**.

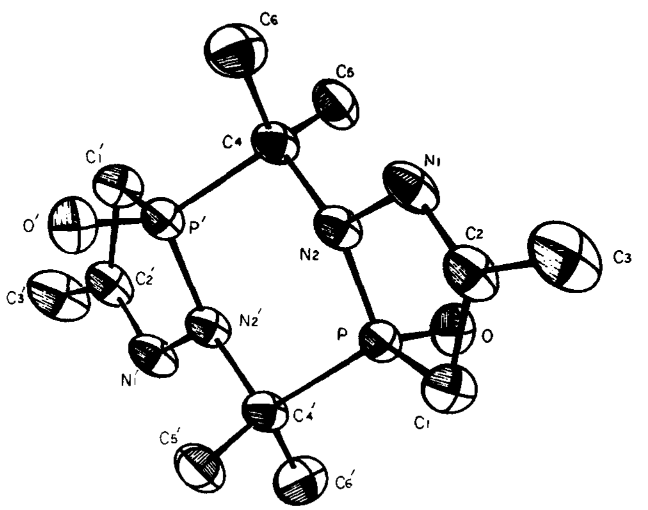


FIGURE 2 Structure of **6** showing the atom numbering scheme. The $AlCl_3$ units are omitted for clarity.

X-Ray Structure Analyses of **4** *and* **6**

Suitable single crystals of **4** and **6** were obtained as described above. Initial lattice parameters were obtained from least-squares fits to 25 reflections, 15° ≤ 2θ ≤ 20°, accurately centered on an Enraf-Nonius CAD-4 automated diffractometer and refined subsequently using higher angle data. Crystal data for **4**: $C_{12}H_{26}AlCl_3N_3OP$, M_r = 392.67, monoclinic space group $P2_1/n$, a = 15.400(6), b = 14.442(4), c = 9.206(3) Å, β = 93.33(3)°, U = 2044 Å^3, D_c = 1.276 g cm^{-3}, Z = 4, λ (MoK_α) = 0.71069 Å, μ (MoK_α) = 5.7 cm^{-1}. Crystal data for **6**: $C_{12}H_{22}Al_2Cl_6N_4O_2P_2$, M_r = 582.96, triclinic, space group $P1$, a = 8.556(1), b = 9.782(1), c = 8.119(1), α = 94.58(1), β = 104.97(1), γ = 78.35(1), U = 642.6 Å^3, D_c = 1.506 g cm^{-3}, Z = 1, λ (MoK_α) = 0.71069 Å, μ = 8.8 cm^{-1}. Totals of 3751 and 2265 unique reflections were collected at 25°C for **4** and **6**, respectively, using the $\theta/2\theta$ scan mode over the range 2.0° ≤ 2θ ≤ 50.0°. Both data sets were corrected for Lorentz and polarization effects. An empirical absorption correction was made in the data set for **4**, but not for **6**. Decay corrections were not necessary for either compound. Both structures were solved by direct methods using 2277 and 1547 reflections with $I > 3\sigma(I)$ for **4** and **6**, respectively. The final residuals were $R = 0.0382$ and $R_w = 0.0373$ for **4** and $R = 0.0524$ and $R_w = 0.0557$ for **6**.

Acknowledgment

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